

Discrepancy between TPD- and FTIR-based measurements of Brønsted and Lewis acidity for sulfated zirconia

Brett T. Loveless¹, Anil Gyanani, Darrin S. Muggli^{*}

Department of Chemical Engineering, University of North Dakota, Grand Forks, ND 58202-7101, United States

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ABSTRACT

Temperature-programmed desorptions (TPD) of isopropylamine (IPA), NH_3 , and pyridine were compared with diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of pyridine to determine the effect of H_2O on the Brønsted and Lewis acidities of two sulfated zirconia (SZ) catalysts. Although the traditional interpretation of pyridine infrared spectra showed an apparent increase in Brønsted acidity upon treating SZ with H_2O , TPD spectra showed that H_2O displaced IPA from approximately one-fifth of the Lewis sites with no corresponding increase in Brønsted acidity. Water treatment prior to TPD displaced similar amounts of both NH_3 and pyridine. The primary effect of H_2O is displacement of weakly adsorbed basic probe molecules from Lewis sites, rather than the conversion of Lewis sites to Brønsted sites. Finally, different types of analyses (e.g. infrared or TPD) of catalyst acidity yield dramatically different conclusions regarding Brønsted and Lewis acidity.

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1. Introduction

Solid acid catalysts, especially strong acids such as sulfated zirconia (SZ), are being studied extensively in an effort to replace liquid-phase acids. Although previous studies [1–3] concluded that acidity is essential for several important catalytic reactions, the correlation between the type of acidity (Brønsted or Lewis) and catalyst activity is debated [4–6]. To complicate the debate on the importance of Brønsted and Lewis acidity, many studies have proposed that water, present in the feed or produced as a reaction product, converts Lewis sites to Brønsted sites. One study determined that the amount of water necessary to optimize catalyst activity [7] depends upon the number of Lewis and Brønsted acid sites. Tierney and coworkers [8] suggested that water converted Lewis sites to Brønsted sites, which increased catalytic activity. Other studies on metal oxides [9,10] indicated that water alone may not produce Brønsted sites that are strong enough to protonate probe molecules but that a combination of sulfation and water treatment is required. Still other studies [4,5] suggested that water converts Lewis sites into Brønsted sites that are inactive for *n*-butane isomerization. Parera [11] observed that

both dry and hydrated SZ catalysts had the same activity in butane isomerization. He questioned, along with Morterra et al. [12], the importance of Brønsted acidity in SZ's catalytic activity. Although previous studies [3,7,13–16] measured the effect of surface hydration on catalyst activity during acid-catalyzed reactions, the activity of catalysts can be understood more fully once the changes in the nature of acidity due to H_2O are determined.

Infrared spectroscopy (IR) has been used extensively to measure catalyst acidity. Infrared spectra of NH_3 showed that dry catalysts contained both Brønsted and Lewis acid sites, and H_2O increased IR bands corresponding to NH_4^+ at the expense of those from NH_3 [17]. This observation led to the conclusion that H_2O converts Brønsted sites to Lewis sites. Another NH_3 IR study [18] found that NH_3 adsorbed on SZ produced IR peaks attributed to both Lewis and Brønsted sites. The authors of this study observed that chemisorbed surface SO_3 groups act as strong Lewis acids, but when the sample was hydrated these species changed structure. They concluded that surface H_2O influences catalytic activity for the isomerization of isobutane. Instead of NH_3 , Morterra et al. [12] used IR spectra of adsorbed pyridine to observe significant Brønsted acidity on highly hydrated SZ systems, although they exhibited no catalytic activity. In cases of low hydration, where the system had good catalytic activity, few Brønsted sites remained and they were unable to interact with strong bases.

In addition to IR methods, temperature-programmed desorption (TPD) has been used to determine the total number of acid

^{*} Corresponding author.

E-mail address: darrin_muggli@und.nodak.edu (D.S. Muggli).

¹ Current address: Department of Chemical Engineering, University of California, Berkeley, CA 94720, United States.

sites, their types (Brønsted or Lewis), and their strengths [19]. NH_3 TPD has been used extensively to quantify surface acidity, although its reliability has been questioned due its tendency to adsorb at many sites, even some that are basic [20]. Pyridine TPD has also been used to quantify acid sites [21,22], but steric limitations may exist with the relatively large pyridine molecule.

One drawback of NH_3 and pyridine TPD is that they do not differentiate readily between Lewis and Brønsted sites. Temperature-programmed desorption of alkylamines, however, distinguishes between Brønsted and Lewis sites [23–27]. Alkylamines become protonated at Brønsted sites and form alkylammonium ions, which later decompose to NH_3 and olefins by a reaction similar to Hoffman elimination [28]. Since desorption of both NH_3 and olefin occurs in a narrow temperature range, the strength of Brønsted sites cannot be determined using amine TPD [23–27].

Kulkarni and Muggli [29] utilized TPD and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to investigate the effect of water on the acidity of TiO_2 and sulfated TiO_2 . They found that whereas traditional interpretation of pyridine IR spectra showed an increase in Brønsted acidity with H_2O , isopropylamine (IPA) TPD showed that H_2O displaced IPA from one-third to one-half of the Brønsted sites. The main effect of H_2O was the displacement of adsorbed probe molecules from Brønsted sites, not the conversion of sites from Lewis to Brønsted.

The work presented herein focuses on the effect of water on the acidity of sulfated zirconia using TPD and DRIFTS. Sulfated zirconia, a solid acid catalyst that has been well studied for various acid-catalyzed reactions [30–32], contains both Brønsted and Lewis acid sites. For comparison, this study used two samples of SZ; one that exhibited Brønsted acidity in DRIFTS analysis and one that did not. Temperature-programmed desorption experiments were conducted using IPA, NH_3 , and pyridine as probe molecules. Adsorbing H_2O either before ($\text{H}_2\text{O}/\text{probe}$) or after ($\text{probe}/\text{H}_2\text{O}$) the probe examined the effect of H_2O on catalyst acidity. Pyridine DRIFTS experiments were compared with TPD results. This study represents the first comparison of these measurements of catalyst acidity on SZ.

The purpose of this study is to report the discrepancy between TPD and IR-based measures of Brønsted and Lewis acidity and the dramatic difference in conclusions that each method would produce. The results presented herein show that the method of acid-site determination must be considered when evaluating various studies that report the effects of acidity on reactions catalyzed by sulfated zirconia. The reasons for the difference in the acidity measures, although of great interest, are beyond the scope of this paper.

2. Experimental

2.1. Catalyst preparation

Commercially available sulfated zirconia catalyst (SZ-I) was used as provided (MEL Chemicals, 7.5 mass% SO_3). The other SZ catalyst used in this study (SZ-II) was prepared [30] by treating 1 g of zirconium butoxide (Aldrich, 97%) with 15 mL of a 1.0 N sulfuric acid solution (Fisher Scientific, 93–98%). Subsequent stirring for 15–20 min preceded filtering without washing. The sample was then dried at 373 K for 12 h and calcined in air at 873 K for 3 h before use.

2.2. Temperature-programmed desorption

The TPD system used in this study has been described previously [33]. Approximately 50 mg of catalyst was placed in a 7-mm inner diameter (i.d.) quartz reactor, which was heated by

an electric furnace (Ni–Cr wire). A 0.5-mm chromel–alumel thermocouple measured the temperature at the center of the catalyst bed and provided feedback to the temperature programmer. A Pfeiffer QMS 200 quadrupole mass spectrometer monitored the reactor effluent downstream via a fused silica capillary. Mass spectrometer signals were calibrated by injecting known volumes of IPA, NH_3 , pyridine, propene, and water into the gas flow downstream of the reactor.

To create a reproducible surface, the catalyst was heated, at a rate of 1 K/s, to 723 K and held at that temperature for 15 min in 200 sccm of 20% O_2 in He (UHP). Subsequently, gas flow switched to 200 sccm He (UHP) as the catalyst cooled to room temperature. The catalyst surface was then saturated by pulsing 3 μL isopropylamine (99.5%, Aldrich), 3 μL pyridine (99.9%, Aldrich), or 3 mL NH_3 (99%, Matheson). Helium flowed for approximately 45 min following the final pulse to flush gas-phase and physisorbed species from the catalyst surface. After flushing, TPD ensued at a heating rate of 1 K/s. The catalyst was held at the final temperature of 723 K for 15 min to ensure complete desorption of products. Experiments with coadsorbed water followed the same procedure with the addition of three 1 μL pulses of water, injected either before or after injection of the basic probe molecule.

2.3. DRIFTS equipment and procedures

Infrared analysis employed a FTIR spectrophotometer (Thermo Nicolet 670) equipped with a MCT-A detector cooled by liquid nitrogen. The apparatus consisted of a Praying Mantis DRIFTS accessory (Harrick Scientific, DRP) that housed a reaction cell (Harrick Scientific, HVC-DRP) equipped with a heater, a sample cup that held approximately 0.2 g of catalyst, and a dome with one quartz and two KBr windows. A purge-gas generator (Parker Balston 7545 NA) provided dry air for system purge. A mass flow controller delivered 100 sccm He or 20% O_2 in He (UHP, Praxair) to the reaction cell.

To create a clean surface for DRIFTS analysis, the catalyst was heated in 20% O_2 in He to 723 K and this temperature was maintained for 20 min. Thereafter, the catalyst was cooled to room temperature and Omnic software (Thermo Nicolet) collected background spectra of the clean surface. After background collection, three 1 μL pulses of pyridine saturated the catalyst surface. The spectrophotometer collected room-temperature spectra at 10, 30, and 60 min after pyridine injection. For water coadsorption experiments, the above procedure was repeated with the addition of three 1 μL pulses of water either before or after pyridine adsorption, with 10 min between injections. To determine changes in acid sites due to desorption of H_2O and pyridine, the temperature was raised to 400 K and then cooled to room temperature before collecting another spectra. The same procedure followed for temperatures of 500, 600, and 700 K.

3. Results and discussion

3.1. TPD of probe molecules

Previous work has employed TPD of NH_3 [29,34–41], pyridine [29,35,42–44], and isopropylamine (IPA) [22,24,29,45,46] to quantify acid sites on catalysts. Figs. 1–3 show TPD spectra of NH_3 , pyridine, and IPA, respectively, on SZ-I. Each figure contains desorption profiles from dry catalysts, surfaces in which water was adsorbed before the basic probe ($\text{H}_2\text{O}/\text{probe}$), and those in which water was adsorbed last ($\text{probe}/\text{H}_2\text{O}$). The TPD profiles from SZ-II are not shown here, as these curves were nearly identical in shape to those from SZ-I; desorption amounts from SZ-II were less than

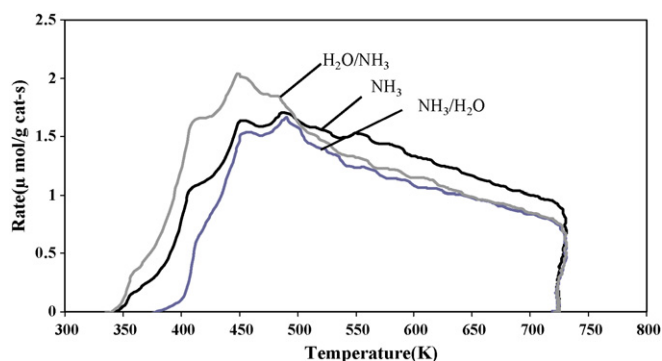


Fig. 1. NH_3 desorption rates during TPD of NH_3 , $\text{NH}_3/\text{H}_2\text{O}$, and $\text{H}_2\text{O}/\text{NH}_3$ on SZ-I.

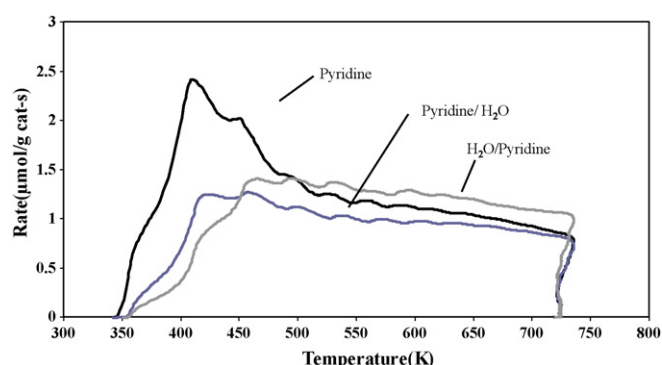


Fig. 2. Pyridine desorption rates during TPD of pyridine, pyridine/ H_2O , and $\text{H}_2\text{O}/$ pyridine on SZ-I.

those of SZ-I for all probe molecules, presumably due to a lesser surface area of this catalyst.

Desorption of NH_3 (Fig. 1) started at approximately 350 K, increased rapidly to a maximum near 450 K, and subsequently decreased throughout the remainder of the experiment, resulting in approximately 580 μmol NH_3/g catalyst desorbed (Table 1). The broad desorption temperature range reveals a wide variation in strengths of acid sites. One limitation of NH_3 TPD is the difficulty in resolving and quantifying Lewis and Brønsted sites; the broad desorption curve in Fig. 1 shows that the desorption peaks from Lewis and Brønsted acid sites were not resolved. That is, NH_3 TPD was not sensitive enough to differentiate between the two types of acid sites [28,29,37,40,47].

Fig. 2 shows desorption of pyridine from SZ-I. Desorption began at 350 K and reached a maximum rate near 410 K before

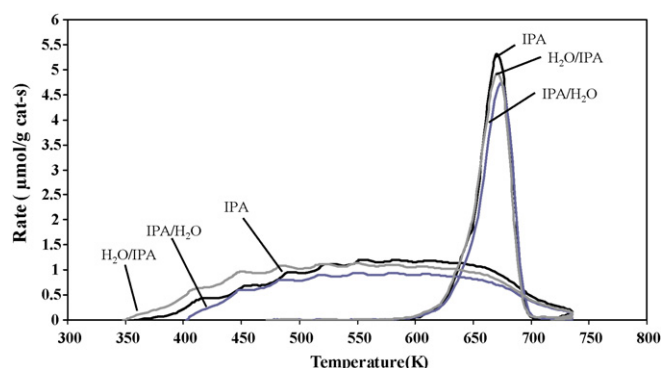


Fig. 3. Propene (peaks at 600–700 K) and IPA (broad peaks at 350–723 K) desorption rates during TPD of IPA, IPA/ H_2O , and $\text{H}_2\text{O}/$ IPA on SZ-I.

Table 1

NH_3 and pyridine desorption amounts ($\mu\text{mol}/\text{g}$ catalyst) during TPD with and without co-adsorbed H_2O

	SZ-I	SZ-II
NH_3	580 ± 30	250 ± 30
$\text{NH}_3/\text{H}_2\text{O}$	450 ± 10	200 ± 10
$\text{H}_2\text{O}/\text{NH}_3$	540 ± 50	200 ± 10
Pyridine	580 ± 40	120 ± 20
Pyridine/ H_2O	410 ± 60	100 ± 20
$\text{H}_2\text{O}/$ pyridine	520 ± 60	110 ± 20

decreasing. The desorption temperature range was similar to that of NH_3 TPD, but the maximum desorption temperature was lower for pyridine. Similar to NH_3 , pyridine TPD spectra show no clear distinction between Lewis and Brønsted sites. The amount of pyridine that desorbed during TPD was 580 $\mu\text{mol}/\text{g}$ catalyst (Table 1).

IPA TPD spectra reveal more information than do those of the other probe molecules. According to Gorte [48], Brønsted sites protonate amines to form alkylammonium ions that subsequently decompose to propene and NH_3 above 575 K. Fig. 3 shows that IPA formed propene between 600–700 K via a Hoffman elimination type reaction, in agreement with studies by Gorte et al. [22–24,46,48]. Thus, desorption of propene indicates the presence of Brønsted sites. Unreacted IPA desorbed from both Lewis and Brønsted sites in a broad peak starting at 360 K. Approximately 180 and 280 $\mu\text{mol}/\text{g}$ catalyst of propene and IPA, respectively, desorbed from SZ-I (Table 2).

3.2. Effect of H_2O on TPD spectra

Temperature-programmed desorptions of co-adsorbed H_2O determined the effect of H_2O on the amounts of probe molecules adsorbed on Brønsted and Lewis sites. Co-adsorption experiments were conducted by adsorbing H_2O and probe in different sequences before TPD. That is, H_2O was adsorbed either before ($\text{H}_2\text{O}/$ probe) or after the probe molecule (probe/ H_2O). Table 2 summarizes the amount of propene and IPA that desorbed from samples during TPD of IPA alone, IPA/ H_2O , and $\text{H}_2\text{O}/$ IPA.

All three experiments (IPA alone, IPA/ H_2O , an $\text{H}_2\text{O}/$ IPA) produced similar amounts of propene, indicating that water did not displace IPA adsorbed at Brønsted sites. This also indicates that when IPA was adsorbed after H_2O , it displaced substantially the H_2O that was pre-adsorbed on Brønsted sites. That is, pre-adsorption of H_2O did not change IPA coverage on Brønsted acid sites. Note that the propene TPD amounts provide no evidence that H_2O converted acid sites from Lewis to Brønsted.

On SZ-I, water displaced IPA adsorbed weakly at Lewis acid sites, reducing significantly the IPA desorbed for IPA/ H_2O compared to IPA alone. The amounts of IPA that desorbed were also the same for $\text{H}_2\text{O}/$ IPA and IPA TPDs, which suggest that IPA also displaced pre-adsorbed H_2O from Lewis sites. These results suggest a competitive adsorption between IPA and H_2O on SZ-I.

Table 2

Desorption amounts of IPA and propene ($\mu\text{mol}/\text{g}$ catalyst) during TPD of IPA, IPA/ H_2O , and $\text{H}_2\text{O}/$ IPA

	SZ-I	SZ-II
IPA	280 ± 50	90 ± 20
IPA/ H_2O	220 ± 20	82 ± 8
$\text{H}_2\text{O}/$ IPA	290 ± 30	71 ± 8
Propene (IPA)	180 ± 20	65 ± 3
Propene (IPA/ H_2O)	170 ± 20	62 ± 3
Propene ($\text{H}_2\text{O}/$ IPA)	170 ± 20	61 ± 4

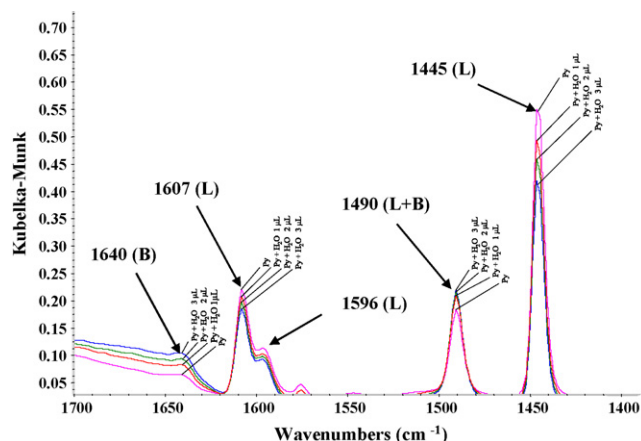


Fig. 4. DRIFTS spectra of adsorbed pyridine on SZ-I with subsequent adsorption of 1 μ L H₂O every hour.

Table 2 shows similar trends for SZ-II, but less clearly due to a relatively large confidence interval for IPA desorption from the dry catalyst.

NH₃ and pyridine desorption amounts in Table 1 (SZ-I) show the same trends as those described above. Adsorbing H₂O prior to the probe molecule produced little or no effect on the amount of desorbed probe molecule during TPD. Injecting H₂O after probe molecule adsorption displaced some of the weakly adsorbed probe molecules. Although the total amount of adsorbed probe molecule varied with the molecule's identity, the percentage of weakly adsorbed probe molecule displaced by H₂O (when H₂O was adsorbed second) was fairly consistent for each experiment. Water displaced 20, 21, and 29% of the adsorbed IPA, NH₃, and pyridine, respectively. Table 1 shows similar trends for SZ-II: water blocks or displaces NH₃ from adsorption sites and it displaces pre-adsorbed pyridine. One possible difference between the two catalysts appears to be that H₂O adsorbs to SZ-II more strongly than SZ-I. For all probe molecules, H₂O blocked adsorption more effectively on SZ-II than SZ-I when H₂O was pre-adsorbed. This can be seen in Tables 1 and 2 by comparing the relative probe desorption amounts between H₂O/probe and probe alone TPDs.

3.3. Pyridine DRIFTS and H₂O

Analyzing the IR spectra of adsorbed pyridine is a widely utilized technique to determine, at least qualitatively, Brønsted and Lewis acidity of catalysts. For SZ, traditional spectral interpretation of adsorbed pyridine attributes absorption peaks at 1607, 1490, and 1445 cm⁻¹ to Lewis, Lewis and Brønsted, and Lewis sites, respectively [40,43,44,49]; other peaks attributed to Brønsted acid sites on sulfated zirconia are 1640, 1610, and 1540 cm⁻¹ [49].

Fig. 4 shows DRIFTS spectra from an experiment in which several H₂O pulses of 1 μ L each were adsorbed at room temperature at hour intervals after SZ-I was saturated with pyridine. This spectrum produced peaks at 1607, 1490, and 1445 cm⁻¹. A shoulder at 1596 cm⁻¹ shows pyridine weakly bonded to Lewis sites (this shoulder disappeared when the catalyst was heated to 400 K and above as shown in Fig. 5). Apparently, H₂O did not displace completely all of the weakly adsorbed pyridine at room temperature.

Fig. 4 shows that peaks at 1607 and 1445 cm⁻¹ decreased with each injection; water appears to reduce the amount of pyridine adsorbed at Lewis sites, in agreement with TPD experiments. The peak representing both Lewis and Brønsted sites in Fig. 4 (1490 cm⁻¹) increased with the first injection of H₂O, and remained constant for the subsequent injections. Absorption peaks generally observed as Brønsted sites on SZ, 1640, 1610, and 1540 cm⁻¹, are either nonexistent or minor peaks in Fig. 4. The broad, unresolved peak near 1640 cm⁻¹ increased with H₂O exposure.

Fig. 5 shows the effect of temperature on pyridine DRIFTS spectra for SZ-I. In these experiments, the catalyst sample was saturated with pyridine, heated to the desired temperature, and cooled to room temperature before gathering spectra. Peak intensities representing both Lewis and Brønsted acid sites decreased with increased temperature as pyridine desorbed from the catalyst surface. SZ-II (not shown) exhibited the same decrease in all peak intensities with temperature. The SZ-II catalyst differed from SZ-I in that pyridine adsorption exhibited the typical Brønsted peaks at 1540, 1610, and 1640 cm⁻¹. Fig. 6 shows the change in peak intensities with five 1 μ L H₂O doses. The only peak that decreased with H₂O dosing was the 1445 cm⁻¹ peak (Lewis). Peaks at 1640 (B), 1610 (B), 1540 (B), and 1490 cm⁻¹ (L + B) all

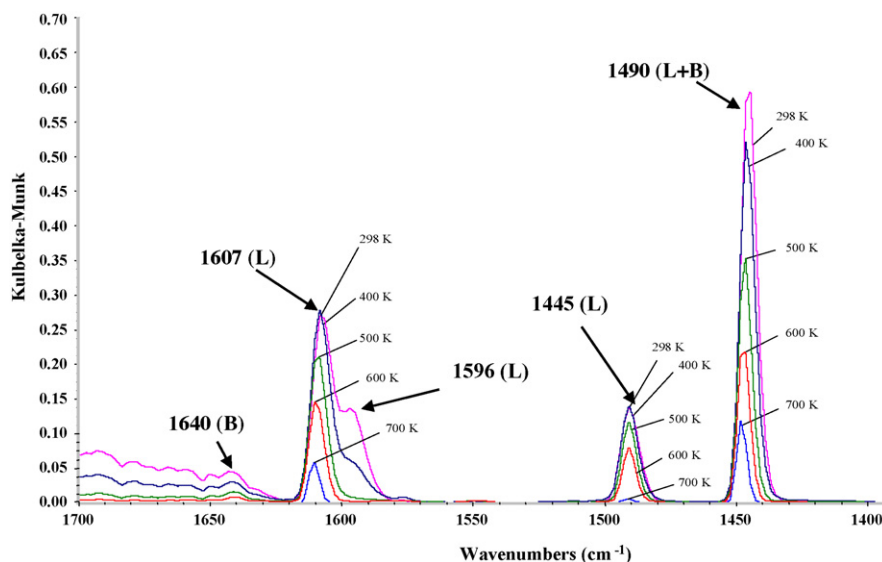


Fig. 5. The effect of temperature on DRIFTS spectra of pyridine adsorbed on SZ-I.

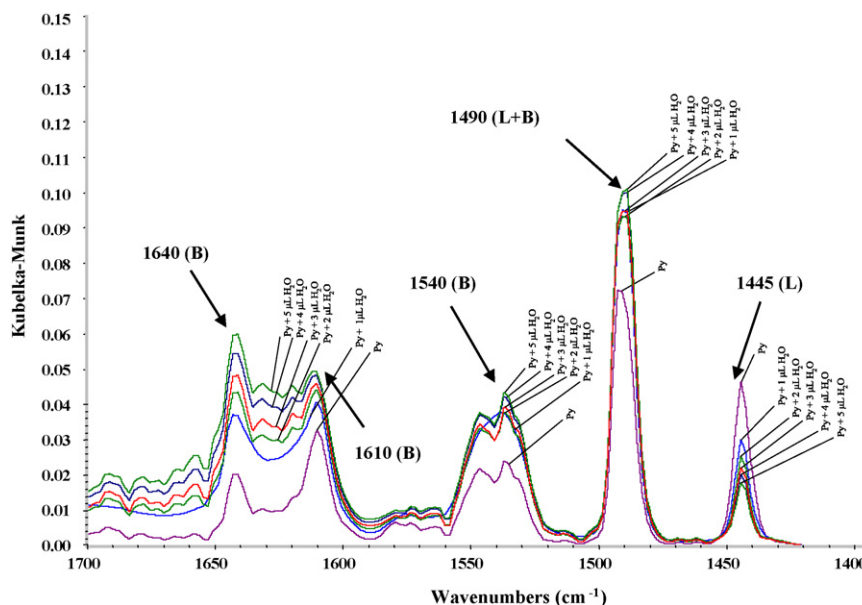


Fig. 6. DRIFTS spectra of adsorbed pyridine on SZ-II with subsequent adsorption of 1 μL H_2O every hour.

increased, with the increase in the first dose of water being significantly larger than any subsequent increases.

To compare the change in Lewis and Brønsted peak intensities with temperature, Fig. 7 compares the 1445 cm^{-1} peak (Lewis) with the 1640 cm^{-1} (Brønsted) on SZ-II. In both panels of Fig. 7, the peak heights, normalized by their respective room-temperature peaks, were plotted against temperature. The linear decrease in the Brønsted peak (1640 cm^{-1}) contrasts the more rapid, exponential decrease of the Lewis peak (1445 cm^{-1}) as temperature increased.

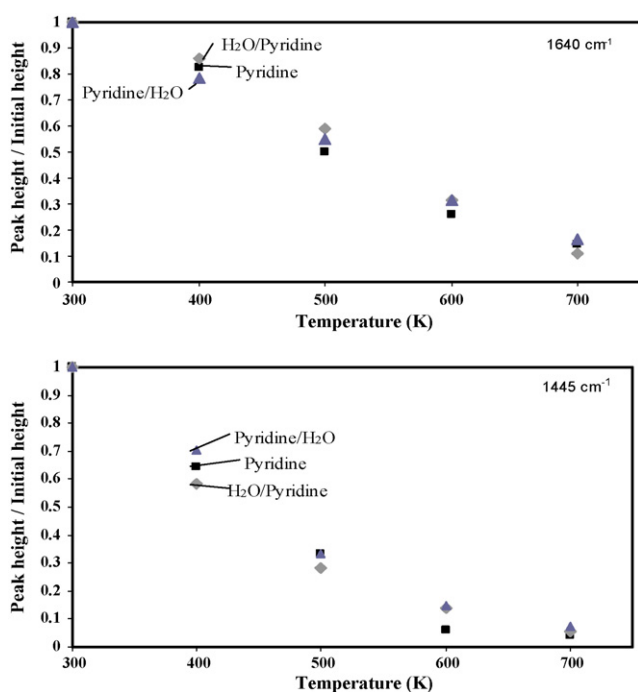


Fig. 7. Change in normalized DRIFTS peak heights upon heating of adsorbed pyridine with and without H_2O . The top panel shows the change in Brønsted acidity (1640 cm^{-1}) whereas the bottom panel shows Lewis sites (1445 cm^{-1}).

3.4. Catalyst comparison

Table 1 shows the desorption amounts of NH_3 and pyridine on both catalysts. The results are noteworthy since the desorption amounts of pyridine and NH_3 are equal on SZ-I. On SZ-II, however, results show that the desorption amount of NH_3 was twice that of pyridine. It was mentioned previously that pyridine, due to its large molecular size and steric limitations, may not be a suitable probe for the estimation of acid site strength and concentrations by TPD in SZ. The difference in the adsorbate coverage is most likely a function of pore structure, as mentioned by Selli and Forni [50]. Small pores can cause adsorption hindrance of bulky molecules on some of the active sites. Therefore, the adsorption of a bulky molecule like pyridine on SZ-I and SZ-II may depend upon the pore structure of the two catalysts.

As mentioned, conventional IR peak assignments would indicate substantially more Brønsted acidity in SZ-II. Results from IPA TPD, however, show that although desorption amounts varied between catalysts, the relative amounts of acid sites did not. The ratio of Brønsted sites (propene desorption amounts) to total sites (propene and IPA) was 0.40 ± 0.05 and 0.43 ± 0.06 for SZ-I and SZ-II, respectively for IPA TPD without H_2O .

3.5. H_2O displacement of molecules at weak Lewis acid sites

Both TPD and DRIFTS results show that H_2O competes for adsorption to weak Lewis sites with all three probe molecules. A shift in IPA desorption temperature appears when comparing IPA/ H_2O and H_2O /IPA runs (Fig. 3); when adsorbed last, H_2O seems to displace weakly adsorbed IPA from Lewis sites. Desorption of IPA in all IPA/ H_2O experiments (SZ-I) began at higher temperatures ($400 \pm 6\text{ K}$) than in H_2O /IPA experiments ($360 \pm 10\text{ K}$). In agreement, the amount of IPA that desorbed when H_2O was adsorbed after IPA was significantly less than that of IPA alone or H_2O /IPA TPDs; these last two experiments exhibited the same IPA desorption amount. This indicates that water displaced some of the weakly bound IPA. Water had no effect on the number of Brønsted sites, however, as the differences in the amounts of desorbed propene in all three experiments were statistically insignificant.

As mentioned previously, NH_3 TPD is a widely used method for catalyst acidity characterization. Ammonia adsorption at both Brønsted and Lewis sites, however, causes difficulties in measuring the populations of different acid sites [28]. Several experiments have been attempted to enhance the ability of NH_3 TPD to measure both Brønsted and Lewis sites. Woolery et al. [47] proposed a method that hydrates the catalyst after it is saturated with ammonia. In this method, water presumably displaces NH_3 from Lewis sites but leaves Brønsted sites unaffected. They added further that the low-temperature ammonia peak can be eliminated by purging ZSM-5 with water-loaded He at 125 °C. The low-temperature peak in Fig. 1, however, does not disappear with H_2O exposure, but H_2O shifted the maximum NH_3 desorption rate from ~450 to 480 K; the same shift occurred in SZ-II (not shown). This indicates that water displaced some, but not all, NH_3 adsorbed at Lewis sites. Similarly, Bagnasco found that the NH_3 desorption peak increased 25–30 °C with the addition of water on Sn/Zr hydrogen phosphate [51]. Bagnasco explained that the addition of water displaces ammonia from some weak Lewis sites. However, since ammonia is a stronger base than water, it will remain adsorbed to Brønsted sites. Although there was a shift in Bagnasco's desorption profile, the amount of desorbed NH_3 was equal in dry and $\text{NH}_3/\text{H}_2\text{O}$ runs. Fig. 1 shows that when H_2O was adsorbed first ($\text{H}_2\text{O}/\text{NH}_3$), the desorption peak shifted to lower temperatures, suggesting NH_3 bound more weakly to the surface compared to NH_3 and $\text{NH}_3/\text{H}_2\text{O}$ runs.

DRIFTS results also show water displaced pre-adsorbed probe molecules at weak Lewis sites. Fig. 4 shows clearly that water displaced pyridine adsorbed at Lewis sites (1445 cm^{-1}). The peak at 1445 cm^{-1} also decreased upon heating to 400 K (Fig. 5), indicating that weakly adsorbed pyridine at Lewis sites contributes to this peak. Also, the signal at 1607 cm^{-1} shows the effect of water on Lewis acidity. Every dose of water (1 μL) decreased the intensity of the 1607 cm^{-1} peak. Some disagreement exists in the literature on the assignment of the 1607 cm^{-1} peak. Wan et al. assigned characteristic bands at 1640, 1610, 1542 and 1490 cm^{-1} to pyridinium ions adsorbed on Brønsted sites [49]. The bands at 1607, 1575, 1490 and 1445 cm^{-1} correspond to pyridine adsorbed on Lewis acid sites [49]. A few studies [40,52,53] assigned the peak at 1607 cm^{-1} to pyridine adsorbed at Brønsted sites. Although these three papers based this band assignment on the work of Wan et al. [49], Wan and co-workers in fact assigned the 1607 cm^{-1} peak to pyridine at Lewis sites. Moreover, other research has agreed with this Lewis assignment [12,21]. In this study, the decrease in the intensity of the 1607 cm^{-1} peak with hydration (Fig. 4) suggests it represents Lewis sites, as a similar decrease is seen in the 1445 cm^{-1} peak. The assignment of 1445 cm^{-1} peak to Lewis sites is not debated in the literature [7,40,44,51,52,54]. The effect of water on SZ-II produced a similar decrease in Lewis acidity as DRIFTS analysis shows in Fig. 6.

3.6. The effect of water on the acidity of SZ—discrepancy between TPD and DRIFTS

All TPD results presented herein show clearly that H_2O treatment did not increase the number of Brønsted sites. In general, the traditional interpretation of infrared spectra (Figs. 4–6) however, seem to indicate that H_2O does convert some sites from Lewis to Brønsted.

Morterra et al. [55] concluded that for SZ having both Brønsted and Lewis acidity, the ratio of Brønsted to Lewis sites was not an absolute parameter. Their work suggested that the Brønsted-to-Lewis ratio increases with H_2O surface concentration. This ratio also depended on other factors, including amount of water adsorbed/desorbed, initial calcination temperature, and the

temperature at which the catalyst is outgassed in infrared experiments [42]. A similar study by Li and Gonzalez [52] that studied SZ deactivation during butane isomerization, used pyridine DRIFTS to measure Brønsted and Lewis acidity. Upon addition of water after calcination, they recognized that surface hydration was crucial for catalytic activity. They correlated catalytic activity with the changes in the ratio of Brønsted to Lewis (B/L) sites.

Traditional interpretation of pyridine IR (Fig. 6) on SZ-II clearly indicates that the Brønsted-to-Lewis ratio increased when water was co-adsorbed with the pyridine. DRIFTS results show the Brønsted-to-Lewis ratio, calculated by the ratio of peak intensities at 1540 (B) and $1445\text{ cm}^{-1}\text{ (L)}$, was higher in case of pyridine/ H_2O (1.9) than pyridine alone (0.6), which was later supported by the experiment with multiple H_2O injections (Fig. 4). Table 2 shows, however, that H_2O only displaces weakly adsorbed probe molecules and does not produce any additional Brønsted sites.

Arata [56] examined the isomerization of butane on sulfated zirconia and found the maximum catalytic activity at 350 °C. This activity declined in the temperature range of 400–600 °C. He explained that Brønsted sites, formed by addition of water to Lewis sites, decreased when the catalyst was heated to higher temperatures. Further, he claimed that surface Lewis and Brønsted sites are easily interchangeable by hydration and dehydration. If this explanation holds, one would expect that a H_2O -saturated surface would (1) convert some sites from Lewis to Brønsted and (2) when heated, water desorption would convert the newly created Brønsted sites back to Lewis. Each of these expected consequences is discussed below.

The results of IPA TPDs on SZ-I and SZ-II indicate clearly that water does not convert Lewis sites to Brønsted sites; no increase in Brønsted sites (increased propene desorption) was recorded after adsorption of water. However, traditional interpretation of DRIFTS results of SZ-II appear to agree with Arata as hydration decreased the 1445 cm^{-1} peak (L) and increased the 1540 cm^{-1} peak (B) on SZ-II. Traditional interpretations of SZ-I DRIFTS results may be consistent with Arata, as the 1445 and 1607 cm^{-1} peaks (L) decreased with the concurrent increase of 1490 cm^{-1} peak (B + L) with hydration. The SZ-I results, however, do not produce a compelling conclusion that Brønsted sites were generated from Lewis sites as no strong peaks appeared at 1540 or 1610 cm^{-1} . That is, the acid sites on SZ-I remained primarily Lewis sites regardless of H_2O treatment.

If indeed H_2O converts sites from Lewis to Brønsted and these are easily converted back at higher temperatures due to H_2O desorption, Fig. 7(top panel) ought to show that the Brønsted acidity of hydrated surfaces decreases more quickly with temperature than that of dry SZ. In contrast, Fig. 7(top panel) shows that hydration has no effect on the decrease in Brønsted acidity with temperature. Both TPD and DRIFTS experiments, unless otherwise noted, utilized the same amount (3 μL) of H_2O for all co-adsorption experiments.

4. Conclusions

TPD results of IPA, ammonia, and pyridine revealed the presence of both Brønsted and Lewis acid sites on commercially available (SZ-I) and lab synthesized (SZ-II) sulfated zirconia. The effect of water on the acidity of SZ was determined by co-adsorption experiments, where H_2O was adsorbed either before ($\text{H}_2\text{O}/\text{probe}$) or after the probe molecule ($\text{probe}/\text{H}_2\text{O}$). IPA TPD results showed no increase in Brønsted acidity with hydration, contrary to the traditional interpretation of DRIFTS experiments. TPD results of all basic probes on SZ-I showed that water displaces previously adsorbed molecules from weak Lewis sites.

DRIFTS experiments agreed generally, but not exclusively, with the traditional interpretation of conversion of Lewis sites to Brønsted sites with hydration. SZ-I lacked IR peaks attributed to Brønsted sites, but showed no difference in Brønsted acidity during TPD as compared to SZ-II. Thus, different types of analyses of catalyst acidity can yield dramatically different conclusions regarding Brønsted and Lewis acidity.

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